Information for New Graduate Students
Fall 2012

*Engineering and Chemistry for Sustainable Technology*

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“Sustainable” is not just hugging a tree...
It’s getting everyone to hug a tree
Chemical Engineering and Chemistry 23-Year Collaboration

- Jointly Directed PhD Students
  - 50 Completed
  - 12 In Progress
- ~50 Joint Research Grants
- ~250 Publications and Presentations
- 2004 Presidential Green Chemistry Challenge Award
Current Group – ChEs and Chemists

• Students – All Co-Advised
  ✓ Undergraduates (8 at present)

• Staff
  ✓ Senior Scientists and Postdoctorals – Pamela Pollet, Beth Cope, Rani Jha, Elizabeth Biddinger, Steve Saunders, Andrea Song
  ✓ Coordinator, Deborah Babykin

• Other Collaborators
  ✓ Other GT Students and Faculty
  ✓ Students and Faculty at Other Universities
  ✓ Industry Partners
We Work Together

- Each Problem Has a Team
  - Multilevel, Multidisciplinary
- Each Person Is on Multiple Teams
- Advantages
  - Not All Problems Are Four Years
  - Facilitates Communications
  - Able to Do High Risk, High Return Research

Michelle Kassner, PhD ChBE, 2008, Chevron; Tori Blausucci, PhD ChBE, 2009, ExxonMobil
What Do We Do – and Why?

• Tunable Solvents
  ✓ Supercritical Fluids
  ✓ Nearcritical Fluids
  ✓ Gas Expanded Fluids

• Smart Solvents

• Advantages
  ✓ Benign
  ✓ Better Transport Properties
  ✓ Facilile Downstream Processing
Examples of Sustainable Technology

• Goals
  ✓ Environmentally Benign
  ✓ Cost-Effective

• Energy Applications
  ✓ CO₂ Recovery from Flue Gas
  ✓ Benign Harvesting of Sands and Oil Shale

• Green Pharmaceuticals
  ✓ Continuous Reactions for Pharma
  ✓ Benign Reactions in Nearcritical Water
  ✓ Coupling Reaction + Separations
    ❖ Homogeneous Catalyst Recycle

Heather Patrick, PhD ChBE, 2000, Emory University
Example: Smart Solvent Replacement for Supersolvent -- DMSO

- **Product Isolation from DMSO**
  - Add water, precipitate
  - Extract with another organic

- **Problems with DMSO Removal**
  - Isolation is product dependent.
  - Contaminated aqueous waste
  - No solvent recycling

- **Smart Solvent – Changes Properties on Command**
  - As good as DMSO
  - Decomposes into Volatile Fragments on Command
  - Easy to Remove
  - Can be Reformed and Recycled Later

\[ \text{Dimethyl sulfoxide} \]

\[ \text{H}_3\text{C} \underset{\text{S}}{\text{O}} \underset{\text{O}}{\text{CH}_3} \]
DMSO-like Solvent Has “Built-In” Recycle

Pipyrlene Sulfone

- Solvent Properties Comparable to DMSO
- T-Based Switch, Decomposition ~110°C
- Reaction is Reversible
- Equilibrium and Rates Are Good
Potential Process Cycle
Extraction or Reaction with Smart Solvent

Feed
Dissolution or Reaction Occurs in Polar, High-Boiling Solvent

Return Reformed Solvent

Reverse Reaction Reformulates Polar, High-Boiling Solvent

Bleed Gaseous Solvent Fragments From Separator

Solvent Decomposes to Low-Boiling Fragments

Withdraw Product
Example: Reversible Ionic Liquids

$CO_2$ Switch, Reverse by Heat

$N_2 \rightarrow CO_2$ or heat

$CO_2 \rightarrow N_2$ or heat

Non-polar Liquid

Ionic Liquid
Process: Claisen-Schmidt Reaction and Separation Using Reversible Ionic Liquid

1- Pentane, MeOH; MgSO₄

2-CO₂

RECYCLE

REFORMATION

TMBG

Ionic Liquid

Pentane
CO$_2$ Recovery from Power Plants Using Single-Component Silyl RevILs

- Dual Mechanism Solvent Absorption
  - Chemical Absorption
    - By Reaction of CO$_2$ with RevILs
  - Physical Absorption
    - By Dissolution of CO$_2$ in RevILs
- Increases Capacity
  - Better Separation with Less Energy Penalty
ASPEN Flow Sheet

- Industry Standard Design Software
- Permits Process Alternatives, Optimization
- Calculates Flows, Rates, Energy, Economics

### Simulation Results

<table>
<thead>
<tr>
<th></th>
<th>$ per ton of CO₂ removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Costs</td>
<td>4.50</td>
</tr>
<tr>
<td>Regeneration Energy</td>
<td>3.61</td>
</tr>
<tr>
<td>(Steam)</td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>4.06</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>0.87</td>
</tr>
<tr>
<td>Materials</td>
<td>2.16</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>15.20</strong></td>
</tr>
</tbody>
</table>
Nearcritical Water: A Benign Solvent

- Research Partner: Lilly
- Water at 250-350º C
  - Like Acetone
  - Dissolves both Salts and Organics
- Natural Acid (Base)
  - Catalyzes Reactions
  - Eliminates Waste
- Facile Processing
  - Homogeneous Reactions
  - Separation by Cooling

\[ H_2O \xrightleftharpoons[K_w]{\text{275ºC}} H^+ + OH^- \]

![Graph showing log Kw vs temperature](image-url)
**Gas-Expanded Liquids (GXLs)**

**Tunable Organic-CO$_2$ Mixtures**

- Good Organic Solvents Miscible with CO$_2$
- Solubility is Pressure Tunable
- Solvent properties are pressure tunable
- Separation by Depressurization

Add CO$_2$
Homogeneous Catalyst Recycle with GXLs

- Homogeneous Catalysts
  - Selectivity, Rates
  - Asymmetric Synthesis
  - Difficult to Reuse
- Paradigm
  - Homogeneous Reaction
  - Change Phase Behavior for Separation
- “Designer” Solvents
- “Designer” Catalysts

Megan Donaldson, PhD ChBE 2008, Dow; Nicole Hess, BS ChBE 2008, Berkeley
**CO$_2$ Induced Immiscibility:**
Organic Aqueous Tunable Solvents (OATS)

- Homogeneous Reaction
  - ✓ Organic/Aqueous Solution
  - ✓ Ambient Pressure
- CO$_2$ Induces Phase Split
- GXL Poor Solvent for
  - ✓ Ionic Catalysts
  - ✓ Enzymes
- Decant, Depressurize
  - ✓ Catalyst Recycle
  - ✓ Product Purification
OATS for Biocatalytic Synthesis and Purification of Hydrophobic Drugs

- Enantioselective Biocatalysis
  - Water Insoluble Substrates
  - Facile Product Isolation and Catalyst Recycle

- OATS Mixture
  - Benign Alternative for Organics
  - Higher Enantioselectivity
  - Higher Efficiency
  - Higher Stability of Enzymes
  - Facile Purification of Pharmaceuticals

James Brown, PhD, ChBE, 2000, ExxonMobil; Jason Hallett, PhD, ChBE, 2002, Imperial College, London
**Typical Projects: Recent Grants**

- NSF, Application of Reversible Ionic Liquids
  - Coupling Reactions and Separations
- AMPAC, Many Topics
  - Novel Routes to Pharma
  - Specialty Chemicals
  - Flow Reactors
  - Heterogeneous Catalysis
- NSF, Corning
  - Flow Reactors for Pharma
- Lilly, Applications to Pharmaceuticals
  - DMSO Substitute
  - Reactions in NCW
- DOE and ConocoPhillips, CO$_2$ Capture
  - Single-Component Reversible Ionic Liquids
  - Silylation
  - Molecular Design
- PRF, Smart Solvents for Nanoparticles
- Dow, Polymers
  - PVC Reactions
- Dow, Smart Solvents
  - Gas-Expanded Liquids for Pharma
  - Catalyst Recovery and Recycle
  - Recyclable DMSO Replacement
  - Phase Transfer Catalysis
Finishing the Degree

• Interviewing -- A full-time job
• Connections and Recommendations
• Average time for PhD = 4.3 years
• Typical Pattern
  ✓ ~1/3 Academic Employment
  ✓ ~2/3 Industrial Employment

Greg Marus, PhD ChBE 2011, Albemarle
Recent PhDs from Research Group
In Chemistry and Chemical Engineering

• 2007
  ✓ Charu Panday, SW Research
  ✓ Susanta Samanta, Milliken
  ✓ Liz Hill, Rohm & Haas
  ✓ Laura Draucker, EPA
  ✓ Ejae John, U. Trinidad
  ✓ Jack Ford, U. Kansas

• 2008
  ✓ John Gohres – Evonik
  ✓ Megan Donaldson – Dow
  ✓ Reagan Charney – Law Firm
  ✓ Michelle Kassner – Chevron

• 2009
  ✓ Tori Blasucci – ExxonMobil
  ✓ Kristin Kitagawa – BASF

• 2010
  ✓ Hillary Huttenhower – Pratt and Whitney
  ✓ Ryan Hart -- Exponent
  ✓ Ali Fadhel – GE

• 2011
  ✓ Greg Marus -- Albemarle
Decision Process – Pick a Group

• Research Goals
  ✓ Education
  ✓ Satisfaction
  ✓ Personal Growth

• You Should Seek
  ✓ Enthusiasm
  ✓ Motivation
  ✓ Creativity

• We Seek
  ✓ Molecular Viewpoint
    ❖ Heavy on Chemistry
  ✓ Teamwork
    ❖ Multidisciplinary Approach
  ✓ PhD degree
  ✓ Experiment + Modeling
  ✓ Enthusiasm, Motivation, and Creativity
If You Might Be Interested in Joining Us

• Talk to the Professors
  ✔ Chuck Eckert, 2206 ES&T, 4-7070
    ❖ Coordinator, Deborah Babykin, 2301 ES&T, 4-3690
  ✔ Charlie Liotta, 2201B MS&E, 5-3111
    ❖ Coordinator, Michele Yeager, 2201C MS&E, 4-8222

• Talk to the Students
  ✔ All in the NW Wing, Level 2, ES&T
  ✔ Go in any office and ask for a tour

• Come to our Group Meetings